

Spectroscopic Study of Molecular Interactions in the Binary Mixture of Ethylacetoacetate and Tetrahydrofuran

PRIYANKA YADAV¹ and RAJEEV YADAV^{*2}

¹Department of Chemistry,
Narain (PG) College Shikohabad, U. P., INDIA.

^{*2}Department of Chemistry,
Indian Institute of Technology Kanpur, Kanpur, U. P., INDIA.

(Received on: September 10, 2013)

ABSTRACT

Present study is devoted to understand the molecular interactions in EAA-THF binary liquid mixture using steady-state UV-Vis and fluorescence spectroscopy, fourier transform infrared spectroscopy (FT-IR) and proton-nuclear magnetic resonance (¹H NMR) measurements. The deviation in the absorption as well as emission maximum of R6G in EAA-THF binary mixture has been explained in terms of molecular interactions between solvent molecules in the ground as well as excited state, respectively. The increase in the stretching frequency of carbonyl group of EAA in presence of THF as well as the observed ¹H NMR chemical shift in the upfield region in EAA-THF binary mixture have also been used to explain the molecular interactions in the binary liquid mixture.

Keywords: Binary mixture, Molecular interactions, Ethylacetoacetate, Tetrahydrofuran and Rhodamine 6G.

1. INTRODUCTION

On mixing the different solvents, the unique behaviour of binary mixture compared to its constituent counterpart is believed to be arise from the nature of solvent-solvent interaction. On this purview, the interaction in binary liquid mixtures is a subject of great interest among the

researchers from last few decades¹⁻¹⁸. Many of the researchers have been explained it in terms of acoustic as well as excess acoustic parameters¹⁻¹¹. Spectroscopic methods have also been used to rationalize the nature and extent of molecular interactions in binary liquid mixtures¹²⁻¹⁷. Parveen and co-workers have studied the molecular interaction in the binary mixtures of tetrahydrofuran (THF)

with methanol and o-cresol. They have observed that specific strong interactions are taking place in THF-o-cresol mixture while dispersive forces are responsible for behaviour of THF-methanol mixture¹⁸. Yadava and co-workers have also measured the excess molar volume for binary mixture of nitro-alkanes and 4-methyl-2-pentanone with hydrocarbons and showed the importance of steric factors for molecular interactions in binary liquid mixtures^{7,8}. In the previous work, we have studied the interaction behaviour of ethylacetoacetate (EAA) with chloroform and dimethyl sulfoxide (DMSO) using excess acoustic parameters and spectroscopic methods. In these excess parameters a positive deviation was observed in CHCl₃-EAA binary mixture, whereas a slight negative deviation was found for EAA-DMSO binary liquid mixture. These deviations were explained in terms of molecular interactions between like and unlike molecules using spectroscopic methods⁹. Recently, Sen and co-workers have observed the strong synergistic solvation in binary solvents of primary alcohol and chloroform mixture and showed that the weak hydrogen bond interactions are responsible for such solvation¹².

It is to be noted that people have used fluorescent molecules (solvatochromic dyes) such as coumarine dyes, 4-aminophthalimide, rhodamine 6G and p-nitroaniline etc, when they employ UV-Vis and fluorescence spectroscopic methods^{12, 19}. The solvatochromic behaviour of these molecules can be determined in terms of the stabilization of its electronic energy level. More the polar solvents more will be the stabilization of electronic energy level of a solvatochromic dye and vice versa. The

interaction behaviour in binary solvent mixtures depends on the proportion of either one or both constituting solvents by specific and non-specific interactions¹²⁻¹⁵. These specific and non-specific interactions are mainly hydrogen bonding, self association, dipole-dipole interactions, dielectric enrichments etc^{15-17,20}. The phenomenon, where both the constituent counterpart in the binary mixture solvate the molecules together by mutual interaction and forms completely different solvation shell around the molecules than either of the pure solvent, is termed as Synergism²¹. Apart from synergism, there is a well known phenomenon preferential solvation, where either one of the solvent in the binary liquid mixture, solvate the molecules predominantly through specific and non-specific solute-solvent interactions¹².

In the present work we have studied the interaction behaviour of ethylacetoacetate (EAA) with tetrahydrofuran (THF) by using steady state UV-Vis and fluorescence spectroscopy, Fourier transform infrared spectroscopy (FT-IR) and proton-nuclear magnetic resonance (¹H NMR) measurements.

2. EXPERIMENTAL SECTION

Ethylacetoacetate (EAA) for synthesis, used after distillation and tetrahydrofuran (THF) HPLC grade have been purchased from Merck, India and Rhodamine 6G (R6G) was purchased from Sigma-Aldrich, USA.

The steady state absorption and emission spectra were recorded in a commercial UV-vis spectrophotometer (Shimadzu 2450) and

spectrofluorometer(Fluoromax 4, JobinYvon) respectively using a 10 mm quartz cuvette. FT-IR spectra have been measured by FTIR, PerkinElmer, USA. ^1H NMR spectra of the samples were measured by commercial spectrometer JEOL, ECX-400, Japan operating at 400 MHz and tetramethylsilane was used as reference. All the experiments have been performed at room temperature.

3. RESULTS AND DISCUSSION

3.1 Steady-state UV-Vis and Fluorescence Spectroscopic Study

The absorption and emission spectra of 1 μM R6G have been recorded in pure EAA and THF and their mixtures different compositions of the solvents and are shown in figure 1a and 1b. Here we have taken very small concentration of R6G to avoid solute-solute interactions so that we can get the information of solvent-solvent interaction more precisely. The absorption spectrum of R6G in pure THF and EAA shows an absorption maximum at 534 nm and 528.8 nm respectively. However the emission maximum has been observed as 550.5 nm and 554 nm in pure THF and EAA respectively. Figure 2a shows the change in the absorption maximum of R6G as a function of mole fraction of THF in EAA-THF binary mixture. Here the change in the absorption maximum of R6G in EAA-THFmixture on increasing the mole fraction of THF is not linear. It shows a deviation towards shorter wavelength side in EAA-THF binary mixture. The change in the emission maximum of R6G in the binary mixture also shows a deviation towards shorter wavelength as shown in figure 2b.

Here it is to be noted that the absorption is a ground state phenomenon and the emission is an excited state phenomenon. Hence the change in the absorption and the emission spectrum will be due to the change in the ground and in excited state of R6G, respectively. The dipole moment of R6G is higher in the excited state than the ground state, which perturb the system, hence the deviation in the absorption maximum (figure 2a) is more than that in the emission maximum (figure 2b)¹⁹. In both cases the shift towards blue edge is in between pure solvents showing the preferential solvation of R6G. It shows that, there is a small reduction in the polarity of EAA-THF mixtures. It is to be noted that the polarity of the binary solvent mixture depends on the molecular interactions between the solvent molecules as it decreases with decrease in the molecular interactions between the solvent molecules and vice-versa⁹. Consequently, the polarity of the binary solvent system can also be correlated with molecular interactions for the present study. Hence in EAA-THF binary solvent mixture the interactions between the solvent molecules decreased in either state of R6G.

3.2FT-IR and ^1H -NMR Study

Fourier transform infrared spectroscopy (FT-IR) and proton-nuclear magnetic resonance (^1H NMR) spectroscopic study have been carried out, to understand the molecular interactions in the binary liquid mixture of EAA-THF more precisely. Figure 3 shows the change in the stretching frequency of carbonyl group of ethylacetoacetate in absence and presence of different compositions of THF. A dual humped stretching band present at 1715.0

cm^{-1} and 1736.2 cm^{-1} is for carbonyl group of pure EAA as shown in figure 3. On addition of THF, it starts shifting towards higher wave number and become 1721.2 cm^{-1} and 1746.6 cm^{-1} in presence of 95 % THF (vol/vol). Here, it can be predicted that the intramolecular hydrogen bonding that exists in enol form in ethylacetoacetate is going to decrease in presence of THF, resulting the decrease in the polarity of the EAA-THF binary mixture as observed in previous section.

The proton NMR chemical shifts for pure THF and EAA as well as the mixture of these solvents are shown in figure 4a, b and c respectively. In pure EAA the observed chemical shift(δ_{obs}) were found to be at

2.2077 (s), 3.4869 (s), 4.16-4.127 (q), 1.246-1.2108 (t). Where, the peak at 3.4869 in pure EAA is corresponds to the proton (H^1) of active methylene group. In presence of 90 % THF (vol/vov) the δ_{obs} of EAA become shifter towards upfield region and were observed at 2.1674-2.1625 (d), 3.4209-3.4136 (d), 4.1393-4.0856 (q), 1.2364-1.2010 (t), respectively. Here, the first two peaks are doublet (singlet in pure EAA) is due to the presence of δ_{obs} of pure THF in the same region. The shifting towards upfield region of all chemical shift of EAA in presence of THF also indicates a change in the extent of molecular interactions in EAA-THF binary mixture.

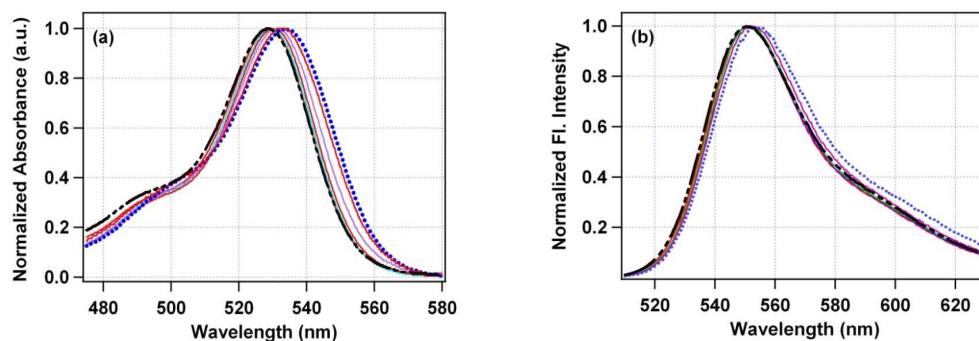


Figure 1. Normalized steady state (a) absorption and (b) emission spectra of R6G in EAA-THF binary liquid mixtures. The absorption and emission spectra of R6G in pure solvents are represented as (— —) for EAA and (.....) for THF.

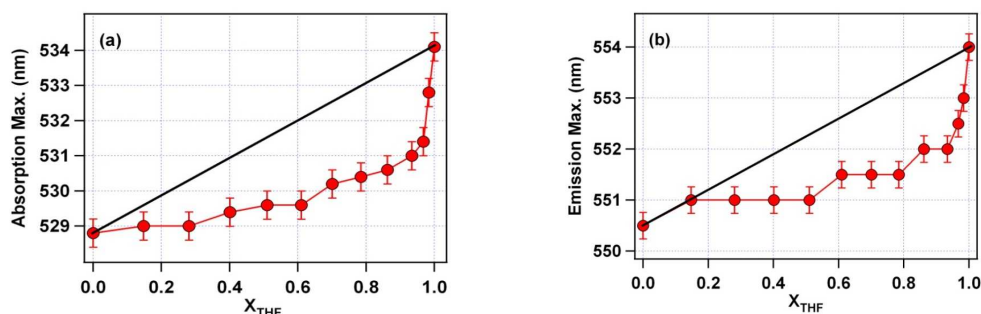


Figure 2. The change in the (a) absorption and (b) emission maximum of R6G with error bars plotted against mole fraction of THF in EAA-THF binary mixtures. Solid black line represents the ideal change.

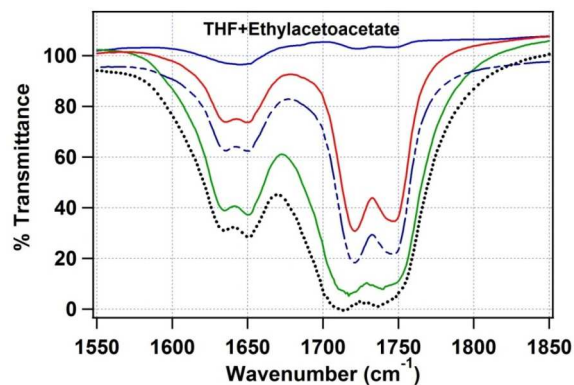


Figure 3. FT-IR stretching bands of carbonyl group of EAA in EAA-THF binary liquid mixture at different compositions. Black dotted, green, blue dashed, red, and blue lines in this figures are for 0 %, 40 %, 90 %, 95 %, 100 % (vol/vol) THF in EAA-THF binary liquid mixtures, respectively.

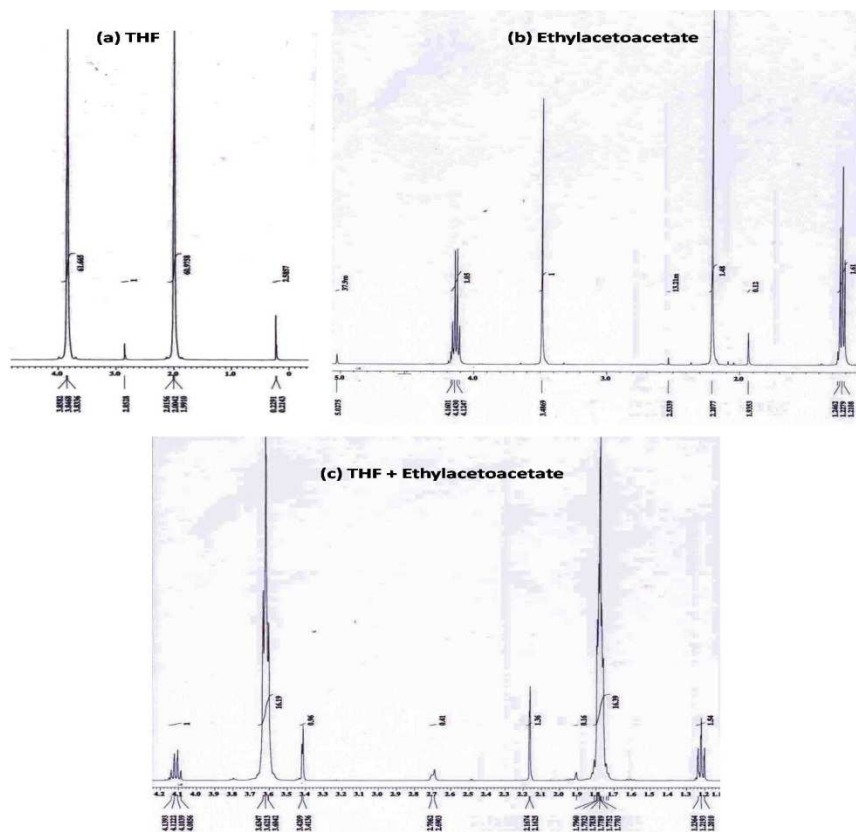


Figure 4. ^1H NMR spectra of (a) pure THF, (b) pure EAA and (c) EAA- THF binary liquid mixtures.

4. CONCLUSION

In the present study, spectroscopic methods have been employed to understand the molecular interactions in EAA-THF binary liquid mixture. The deviation in the absorption as well as emission maximum of R6G towards shorter wavelength in EAA-THF binary liquid mixture has been observed, which causes to decrease in the polarity in the binary mixture to the close proximity of R6G and is responsible for decrease in the molecular interactions between the solvent molecules. The change in the stretching frequency of carbonyl group of EAA towards higher wave number as well as the observed ^1H NMR chemical shift in the upfield region in EAA-THF binary mixture have also been used to explain the molecular interaction in the binary liquid mixtures.

ACKNOWLEDGEMENT

RY thanks University Grant Commission, Government of India for awarding fellowship. We thank central facility of IIT Kanpur for giving the chance to perform the FT-IR and ^1H NMR measurements. We also thank Dr. Pratik Sen, Department of Chemistry, IIT Kanpur for providing the UV-Vis spectrophotometer and spectrofluorometer for absorption and emission measurement, respectively.

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